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Quantitative Measure for the "Nakedness" of Fluoride Ion Sources

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Abstract

A quantitative measure for the donor strength or "nakedness" of fluoride ion donors is presented. It is based on the free energy change associated with the transfer of a fluoride ion from the donor to a given acceptor molecule. Born- Haber cycle calculations were used to calculate both the free energy and enthalpy change for this process. The enthalpy change is given by the sum of the fluoride ion affinity of the acceptor (as defined in strict thermodynamic convention) and the lattice energy difference (ΔU_{POT}) between the fluoride ion donor and the salt formed with the acceptor. Because for a given acceptor, the fluoride affinity has a constant value, the relative enthalpy (and also the corresponding free energy) changes are governed exclusively by the lattice energy differences. In this study, BF_3, PF_5, AsF_5, and SbF_5 were used as the acceptors, and the following seven fluoride ion donors were evaluated: CsF, $N(CH_3)_4F$ (TMAF), N-methyl-urotropinium fluoride (MUF), hexamethylguanidinium fluoride (HMGF), hexamethylpiperidinium fluoride (HMPF), N,N,N-trimethyl-1-adamantylammonium fluoride (TMAAF), and hexakis-(dimethylamino)phosphazenium fluoride (HDMAPF). Smooth relationships between the enthalpy changes and the molar volumes of the donor cations were found which asymptotically approach constant values for infinitely large cations. Whereas CsF is a relatively poor F^- donor [(U_{POT} (CsF) – $U_{POT}(CsSbF_6)$) = 213 kJ mol^{-1}], when compared to $N(CH_3)_4F$ [(U_{POT} (TMAF) – U_{POT}

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($TMASbF_6$)) = 69 kJ mol^{-1}], a four times larger cation (phosphazenium salt) and an infinitely large cation are required to decrease ΔU_{POT} to 17 and zero kJ mol^{-1}, respectively. These results clearly demonstrate that very little is gained by increasing the cation size past a certain level and that secondary factors, such as chemical and physical properties, become overriding considerations.

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Introduction

Although a truly naked fluoride ion cannot exist in either the solid state or in solution, the term "naked fluoride" is frequently applied to fluoride ion sources that exhibit significant solubility in organic solvents.[1-3] Because soluble fluoride ions have given rise to a renaissance in high coordination number chemistry[4,5] and play an important role in many fields, such as halogen exchange[6] and fluorocarbon polymerization reactions,[7] claims for the best or "most naked" fluoride ion source are commonly made. To judge the validity of such claims, a quantitative measure for the "nakedness" is required. Schwesinger[1] and more recently, Mews and coworkers[8] have proposed to use the anion-cation distance or the closest anion-cation contacts in fluoride crystal structures as a measure for the "nakedness." While this approach is reasonable for monoatomic ions, a better method is needed for measuring the "nakedness" of fluoride ions that involve complex cations. In this paper, a quantitative measure based on thermodynamics is proposed and was tested for seven common fluoride ion donors.

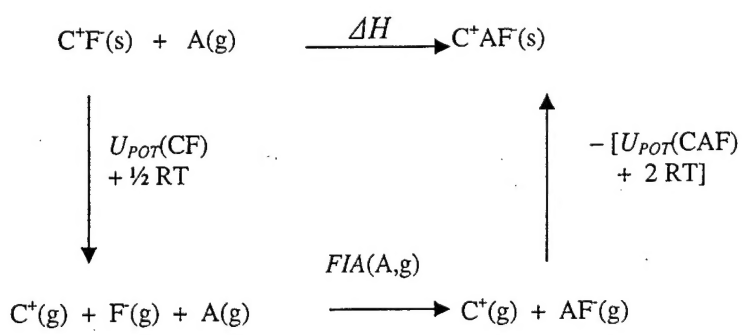
General Description of the Method

The donor ability or "nakedness" of a fluoride ion source can be defined as the ease with which it can transfer a fluoride ion to a given acceptor, A. Because the free energy change, ΔG, is a quantitative measure for the tendency of a reaction to occur,[9] the calculation of ΔG for process (1)

$$C^+F^-\,(s) + A\,(g) \xrightarrow{\Delta G} C^+AF^-\,(s) \qquad (1)$$

provides a quantitative measure for the fluoride donor ability of C^+F^- and hence the "nakedness" of F^- in C^+F^-.

The corresponding enthalpy change, ΔH, of reaction (1) can be determined from the following Born- Haber cycle:

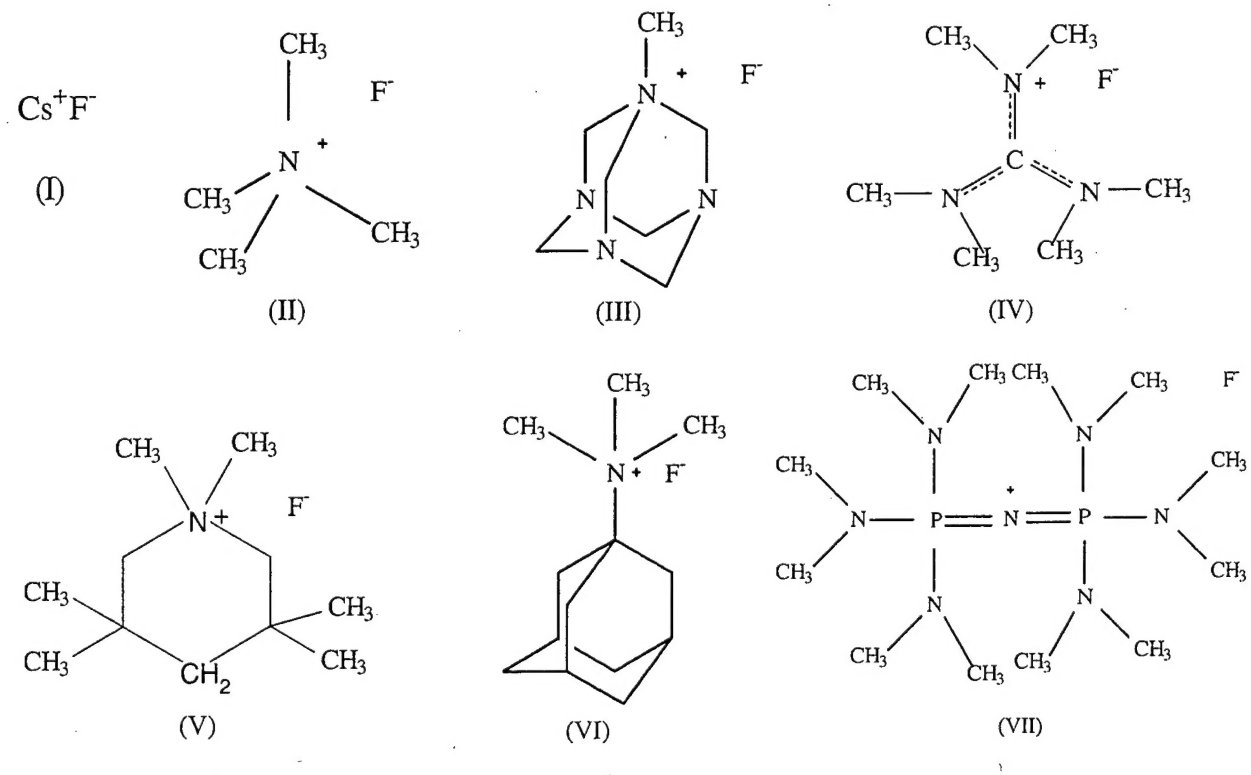


The temperature corrections for the lattice energy, U_{POT}, shown in the above cycle are for polyatomic cations. For a monoatomic cation, such as Cs^+, they become – RT and ½ RT for U_{POT}(CF) and U_{POT}(CAF), respectively, but their sum remains unchanged. The reaction enthalpies for (1) are then given for both polyatomic and monatomic cations by equation (2).

$$\Delta H = U_{POT}(C^+F^-) - U_{POT}(C^+AF^-) - 3/2\,RT + FIA\,(A, g) \qquad (2)$$

Equation (2) shows that for a given acceptor molecule the relative fluoride ion donor strength depends solely on the difference between the two lattice energies. Although the absolute ΔH values depend on the fluoride ion affinity, *FIA*, values,[10] the relative ΔH values should be

similar for different acceptors. This was verified by calculating ΔH for four different Lewis acids; i.e., BF_3, PF_5, AsF_5, and SbF_5. In this study, the following seven fluoride ion donors were evaluated: CsF (**I**), $N(CH_3)_4F$ (TMAF) (**II**),[2] N-methylurotropinium fluoride (MUF) (**III**),[11] hexamethylguanidinium fluoride (HMGF) (**IV**),[12] hexamethylpiperidinium fluoride (HMPF) (**V**),[13] N,N,N-trimethyl-1-adamantylammonium fluoride (TMAAF) (**VI**),[14] and hexakis(dimethylamino)phosphazenium fluoride (HDMAPF) (**VII**).[1]



Estimation of Lattice Energies

The lattice energies[15] of the fluoride salts are estimated using equation (3),

$$U_{POT} = 2I\,(\alpha\, V^{-1/3} + \beta) \qquad (3)$$

where I is the ionic strength of the lattice (= 1, in the case of the C^+AF^- and C^+F^- salts considered in this paper) and α = 117.3 kJ mol^{-1} nm and β = 51.9 kJ mol^{-1}. For this, an estimate of the volume of the cations $V(C^+)$ is required for combination with the anion volumes[16]: $V(F^-)$ =

0.025 ± 0.010 nm^3, $V(SbF_6^-) = 0.181 \pm 0.112$ nm^3; $V(BF_4^-) = 0.073 \pm 0.009$ nm^3 , $V(PF_6^-) = 0.109 \pm 0.008$ nm^3 and, the similar sized $V(AsF_6^-) = 0.110 \pm 0.007$ in order to estimate V in equation (1), taking V(CAF or CF) $= V(C^+) + V(AF^-$ or $F^-)$. The following data were used to estimate the volumes of each cation and the lattice energies of the corresponding fluoride salts.

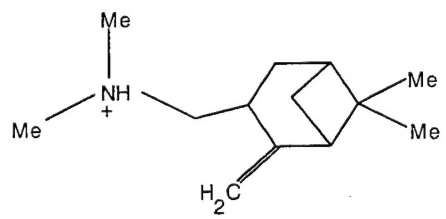
TMAF - ***$N(CH_3)_4^+F^-$(II)*:** The X-ray powder data[2] for tetramethylammonium fluoride, $(CH_3)_4N^+F^-$, (hexagonal, bimolecular cell with $V_{cell}(Me_4NF) = 0.2919$ nm^3) give[17] values of 0.1460 nm^3 and 0.121 nm^3 for the molecular (formula unit) volumes of Me_4NF and Me_4N^+, respectively. Using equation (3), one obtains[16] $U_{POT}(Me_4N^+F^-) = 549$ kJ mol^{-1}.

MUF – ***N-methylurotropinium fluoride, $(CH_2)_6N_4CH_3^+F^-$ (III):*** The crystal structure data[18] for the iodide salt, 1 – methyl – 1,3,5,7 –tetrazatricyclo[3.3.1.1]decan – 1-ium iodide, give $V(C_6H_{15}N_4I) = 0.2527$ nm^3. Subtraction of $V(I^-) = 0.072 \pm 0.016$ nm^3 from this value gives $V(C_6H_{15}N_4^+) = 0.1807 \pm 0.016$ nm^3. Addition of $V(F^-) = 0.025 \pm 0.010$ nm^3 then leads to $V(C_6H_{15}N_4F) = 0.2057 \pm 0.0189$ nm^3 and $U_{POT}(C_6H_{15}N_4F) = U(MU^+F^-) = 501 \pm 11$ kJ mol^{-1}.

HMGF - ***hexamethylguanidinium fluoride, $(Me_2N)_3C^+F^-$, $C_{14}H_{36}N_6^+F^-$ (IV):*** The crystal structure of the hexahydrate of the hexafluorosilicate salt, $[(Me_2N)_3C^+]_2SiF_6^{2-} \cdot 6H_2O$, has been reported.[12] Subtraction of $V = 0.0245$ nm^3 for hydrated water[19] and $V(SiF_6^{2-}) = 0.112 \pm 0.028$ nm^3 yields $V((Me_2N)_3C^+) = ½\{ V([(Me_2N)_3C^+]_2SiF_6^{2-} \cdot 6H_2O) - 6V(H_2O) - V(SiF_6^{2-})] = 0.2021$ nm^3. Addition of $V(F^-)$ leads to $V((Me_2N)_3CF) = 0.2271$ nm^3 and to $U_{POT}((Me_2N)_3CF) = U(HMG^+F^-) = 488$ kJ mol^{-1}.

HMPF - ***1,1,3,3,5,5-hexamethylpiperidinium fluoride, $C_{11}H_{24}N^+F^-$ (V):*** The crystal structure of the fluoride salt has been directly established[13] and leads to $V(C_{14}H_{24}NF) = 0.2874$ nm^3 and $U_{POT}(C_{14}H_{24}NF) = U(HMP^+F^-) = 459$ kJ mol^{-1}.

TMAAF – ***N,N,N -trimethyl-1-adamantylammonium fluoride, $C_{13}H_{24}N^+F^-$ (VI):*** No crystal structure data were given for any salt of this cation.[14] In order to ascertain the likely cation volume and hence estimate a molecular (formula unit) volume for the fluoride salt $C_{13}H_{24}NF$ (VI), the following strategy was used. A search was made of Landolt-Bőrnstein[20] to find compounds containing ions whose elemental composition and overall structural features were close to those of the N,N,N-trimethyl-1-adamantylammonium cation. The closest one found was the 3-N-dimethylaminomethyl-2(10)pinene cation (VI') whose molecular formula is identical ($C_{13}H_{24}N^+$) and for which the crystal structure of its bromine salt has been established.[21]



VI'

Whilst not identical in structural detail to (**VI**), it does contain a bridged CH_2 and the nitrogen moiety outside the pinene ring. The reported structure results in $V(C_{13}H_{24}NBr) = 0.3634$ nm^3. Subtraction of $V(Br^-) = 0.056 \pm 0.014$ nm^3 gives $V(C_{13}H_{24}N^+) = 0.3074 \pm 0.014$ nm^3 which we equate to the volume of the target cation (VI). Adding $V(F^-) = 0.025 \pm 0.010$ nm^3, $V(C_{13}H_{24}NF)$ becomes 0.3324 nm^3 and $U_{POT}(C_{13}H_{24}NF) = U(TMAA^+F^-) = 442$ kJ mol^{-1}.

HDMAPF - ***hexakis(dimethyl-amino)phosphazenium fluoride, $C_{12}H_{36}N_7P_2^+F^-$ (VII):*** The known crystal structure[1] gives $V(C_{12}H_{36}N_7P_2^+) = 0.4755$ nm^3 and $U_{POT}(C_{12}H_{36}N_7P_2F) = U(HDMAP^+F^-) = 399$ kJ mol^{-1}.

Estimation of Reaction Enthalpies and Free Energies from the Born-Haber Cycles

The reaction enthalpies for reaction (1) were estimated for the above seven fluoride ion donors and four Lewis acids using equation (2). Substitution of the *FIA* values in (2) by the Christe/Dixon pF^-, Lewis acidity, values, which are defined by (4)

$$pF^-(A, g) = [-FIA(A, g) / \text{kcal mol}^{-1}] / 10 \quad (4)$$

and their conversion to S.I. units (5)

$$FIA(A, g) / \text{kJ mol}^{-1} = -41.84\ pF^- \quad (5)$$

result in (6).

$$\Delta H = U_{POT}(C^+F^-) - U_{POT}(C^+AF^-) - 3/2\ RT - 41.84\ pF^- \quad (6)$$

Using the published, MP2 based, pF^- values,[22,23] the reaction enthalpies for (1) were calculated, and the results are summarized in Table 1. Conversion of enthalpy, ΔH, to free energy, ΔG, values is achieved by estimation of the corresponding entropy terms $T\Delta S$ using equations (7) and (8),

$$\Delta S = \Delta_f S^0(C^+AF^-, s) - \Delta_f S^0(A, g) - \Delta_f S^0(C^+F^-, s) \quad (7)$$

$$\Delta S = S^0_{298}(C^+AF^-, s) - S^0_{298}(A, g) - S^0_{298}(C^+F^-, s) \quad (8)$$

if the standard entropies of formation of the reactants and products are available or if the standard entropies were known or could be estimated. Neither standard entropies nor standard entropies of formation are available for the salts we have considered, although $S^0_{298}(A, g)$ values are. For ionic solids, however, the recently reported[25] relationship (9) between standard entropy and volume can be used to obtain estimates for $S^0_{298}(C^+AF^-)$ and $S^0_{298}(C^+F^-)$,

$$S^0_{298} = kV \quad (9)$$

where k equals 1360 $JK^{-1}mol^{-1}nm^{-3}$. This leads to equation (10):

$$\Delta S = k\,[V(C^+AF^-, s) - V(C^+F^-, s)] - S^0_{298}(A, g) = k\,\Delta V - S^0_{298}(A,g) \quad (10)$$

where ΔV, which represents the difference between the C^+AF^- and C^+F^- molecular volumes. Due to the additivity[15] of ion volumes, it can also be expressed as:

$$\Delta V = V(AF^-) - V(F^-) \tag{11}$$

The function $[k\ \Delta V - S^0_{298}(A,g)]$ on the right hand side of equation (10) and equal to the entropy change for process (1) can thus be seen to be *independent of the actual choice made for the cation C^+*, and hence the quantitative measure of the "nakedness" of the fluoride ion sources is vested in the enthalpy (rather than the free energy) change for reaction (1). Thus, while ΔG(kJ mol^{-1}) at 298 K for reaction (1) is given by equation (12),

$$\begin{aligned}
\Delta G &= \Delta H - T\Delta S \\
&= U_{POT}(C^+F^-) - U_{POT}(C^+AF^-) - 3/2RT + FIA\ (A, g) \\
&\qquad - 0.298\ \{k\ [V(C^+AF^-, s)] - V(C^+F^-, s)] - S^0_{298}(A, g)\} \\
&= U_{POT}(C^+F^-) - U_{POT}(C^+AF^-) - 3/2RT + FIA\ (A, g) \\
&\qquad - 0.298\ \{k\ [\Delta V] - S^0_{298}(A, g)\}
\end{aligned} \tag{12}$$

separation of terms which are independent on the choice of cation on the right hand side leads to:

$$\begin{aligned}
&[\Delta G - FIA\ (A, g) + 3/2RT + 0.298\ \{k\ [\Delta V] - S^0_{298}(A, g)\}] \\
&\qquad = U_{POT}(C^+F^-) - U_{POT}(C^+AF^-)
\end{aligned} \tag{13}$$

The values of ΔG, obtained in this manner are given in Table 1 and Figure 1. The function: $[\Delta G - FIA\ (A, g) + 3/2RT + 0.298\ \{k\ [\Delta V] - S^0_{298}(A, g)\}]$ would serve as a suitable quantitative measure of our "nakedness" criteria. However it can be simplified. Since the two terms $[\Delta G + 0.298\ \{k\ [\Delta V] - S^0_{298}(A, g)\}]$ within the above function correspond to $[\Delta G + T\Delta S]$ which

equals ΔH, the parameter [ΔH - FIA (A, g) + 3/2RT] (Table 1) can be taken as our quantitative measure for the "nakedness."

These results show that, *independent of the choice of the acceptor molecules*, the relative fluoride ion donor strength decreases in the following order of cations,

HDMAP > TMAA > HMP > HMG > MU > TMA > Cs

and is given by the lattice energy difference between C^+F^- and C^+AF^-. This difference is in turn proportional to the difference of the inverse cube roots of the molecular (formula unit) volumes of the two salts, so that our "nakedness" parameter (14),

$$[\Delta H - FIA\,(A, g) + 3/2RT]\ /\ \text{kJ mol}^{-1} = U_{POT}(C^+F^-) - U_{POT}(C^+AF^-)$$
$$= 2\,\alpha\,[\,V(C^+F^-)^{-1/3} - V(C^+AF^-)^{-1/3}\,] \qquad (14)$$

where α = 117.3 kJ mol^{-1} nm, is governed by the size (volume/nm^3) of the cations and becomes zero for infinitely large cations (i.e., as $V(C^+) \rightarrow$ large, then $V(C^+AF^-) \rightarrow V(C^+F^-)$, $U_{POT}(C^+AF^-) \rightarrow U_{POT}(C^+F^-)$, and so $\Delta H \rightarrow FIA$ (A, g) - 3/2RT).

Using our density-based equation,[26] the difference in lattice energies [$U_{POT}(C^+F^-) - U_{POT}(C^+AF^-)$] can also be equated to (15),

$$[\Delta H - FIA\,(A, g) + 3/2RT]/\ \text{kJ mol}^{-1} = U_{POT}(C^+F^-) - U_{POT}(C^+AF^-)$$
$$= \gamma\,\{[\rho(C^+F^-)/M(C^+F^-)]^{1/3} - [\rho(C^+AF^-)/M(C^+AF^-)]^{1/3}\} \qquad (15)$$

where γ = 1981.2 mol^{-1} cm, and $\rho(C^+F^-)$ and $\rho(C^+AF^-)$ are the densities (in g cm^{-3}), and $M(C^+F^-)$ and $M(C^+AF^-)$] are the chemical formula masses of the respective salts, C^+F^- and C^+AF^-.

The absolute values of the free energy (and enthalpy) change show, as expected, a strong dependence on the fluoride ion affinities of the given acceptor molecules (see Figure 1) and, for infinitely large cations, asymptotically approach these fluoride ion affinity values (adjusted by the RT terms). When the enthalpy values are corrected for the fluoride affinity and RT values of the corresponding acceptors, the individual curves for [ΔH - FIA(A,g) + 3/2 RT]) versus $V(C^+)$

collapse into a single line that asymptotically approaches zero for infinitely large cations (see Figure 2). Because the sign of the lattice energy difference is opposite to that of the fluoride affinity, the salts with the largest cations exhibit the largest (negative) free energy and corresponding enthalpy changes which approach the FIA values, and are the best F^- donors. Therefore, ***the cation size is a suitable measure for the fluoride ion donor strength of a salt.*** Figures 1 and 2 furthermore show that for the hexakis(dimethyl-amino)phosphazenium cation the free energy change already approximates its maximum value (or that the enthalpy change, ΔH, is close to the corresponding FIA value) and that a further increase in cation size[27] will *only minimally* increase the fluoride ion donor strength. Therefore, further synthetic efforts in this direction are hardly warranted, and the potential usefulness of different fluoride ion donor sources will be largely determined by their chemical and physical properties. For example, the tetramethylammonium cation, in spite of its relatively small size, has proven to be extremely useful because of its excellent chemical inertness and oxidation resistance.[2,4] A drawback of this cation, however, is its high symmetry which results in a tendency to undergo disorder that can interfere with crystal structure determinations.[13]

Conclusion

The above analysis shows that for a given acceptor molecule the temperature corrected enthalpy change of reaction (1), or the differences in either the lattice energies, $[U_{POT}(C^+F^-) - U_{POT}(C^+AF^-)]$, or the inverse cube roots of the volumes, $[V(C^+F^-)^{-1/3} - V(C^+AF^-)^{-1/3}]$, or the cube roots of the (ρ/M) terms, $\{[\rho(C^+F^-)/M(C^+F^-)]^{1/3} - [\rho(C^+AF^-)/M(C^+AF^-)]^{1/3}$, all can serve as a reliable measure for the fluoride ion donor strength and hence the "nakedness" of a fluoride ion source. Because for a given acceptor, the enthalpy change depends solely on the molar volume of the cation of the fluoride ion source, the donor strength can easily be predicted.

Acknowledgements

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(10) The process *FIA*(A,g) depicted in figure 1 is *exothermic* and thermodynamically represented by a *negative number*, i.e. *FIA* (A,g) < 0. A convention exists in the literature whereby *FIA* values are cited as *positive values.* Since, in this paper, we will employ our values a*lways in the thermodynamic context* we shall follow the strict thermodynamic convention to avoid confusion. Thus, all *FIA* values cited in this paper are *less than zero* and defined in accordance with a process analogous: $A(g) + F^-(g) \rightarrow AF^-(g)$

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(16) Taken from our single ion volume database table 5 in reference 15.

(17) Using our single ion volume database, the tabulated volume of Me_4N^+ is $V(Me_4N^+) = 0.113 \pm 0.015$ nm^3 which when added to $V(F^-)$ leads to a value $V(Me_4NF) = 0.138 \pm 0.016$ nm^3. Tudela and coworkers (Tudela, D.; Diaz, M.; Alvaro, D. A.; Ignacio, J.; Seijo, L.; Belsky, V. K. *Organometallics* **2001**, *20*, 654) concluded that a value of 0.126 nm^3 for $V(Me_4N^+)$ was more acceptable, which leads to $V(Me_4NF) = 0.151$ nm^3. Taking the average of the two values for $V(Me_4NF)$ then leads to 0.1445 nm^3 which is close to the value found by Christe et. al.[2] It is

interesting to consider volumes derived form other tetramethylammonium halide salts for which structural data are available: Me_4NCl (phase III, tetragonal, Pistorius, C. W. F. T.; Gibson, A. A. V. *J. Solid State Chem.* **1973**, *8*, 126) leads to $V(Me_4NCl) = 0.1565$ nm^3 and $V(Me_4N^+) = 0.1095$ nm^3; Me_4NBr (Duforcq, J.; Haget-Bouillard, Y.; Chanh, N. B.; Lemanceau, B. *Acta. Cryst.* **1972**, *B28*, 1305) leads to $V(Me_4NBr) = 0.1644$ nm^3 and $V(Me_4N^+) = 0.1084$ nm^3; Me_4NI (Christe, K. O.; Wilson, W. W.; Bau, R.; Bunte, S. W. *J. Amer. Chem. Soc.* **1992**, *114*, 3411) leads to $V(Me_4NI) = 0.1824$ nm^3 and $V(Me_4N^+) = 0.1104$ nm^3; Me_4NN_3 (Wilson, W. W.; Christe, K. O.; Feng, J-A.; Bau, R. *Canad. J. Chem.* **1989,** *67*, 1898) leads to $V(Me_4NN_3) = 0.1669$ nm^3 and $V(Me_4N^+) = 0.1089$ nm^3; Me_4NHF_2 (Wilson, W. W.; Christe, K. O.; Feng, J-A.; Bau, R. *Canad. J. Chem.* **1989,** *67*, 1898) leads to $V(Me_4NHF_2) = 0.1558$ nm^3 and $V(Me_4N^+) = 0.1088$ nm^3. The value of $V(Me_4N^+)$ obtained from the fluoride salt is therefore slightly anomalous, and the overall (averaged) value of $V(Me_4N^+) = 0.1112$ nm^3 is close to the value cited in our database.[15,16] This cation is reported to be many orders of magnitude more stable than conventional organic cations towards nucleophiles.[3]

(18) Ribár, B.; Mészáros, C.; Vladmiov, S.; Živanov-Stakić, D.; Golič, L. *Acta. Cryst.* **1991,** *C47*, 1987.

(19) Jenkins, H. D. B.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 4378.

(20) Landolt-Bőrnstein, New Series, Ed: Hellwege, K-H.; Madelung, O. Group III, Crystal and Solid State Phys., Vol 10, *Structure Data of Organic Crystals*, Berlin: Springer-Verlag, 1985.

(21) (a) Kutschabsky, L. *Z. Chem.* **1969**, *9*, 31; (b) Kutschabsky, L. Z.; Reck, G. S. *Prakt. Chem.* **1971,** *312*, 896.

(22) Christe, K. O.; Dixon, D. A.; McLemore, D.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *J.Fluorine Chem.* **2000**, *101*, 151.

(23) Recently, the value of the fluoride ion affinity, *FIA,* of $SbF_{5,g}$ has also been estimated from lattice energies [24]. The value, - 506 ± 63 kJ mol $^{-1}$, corresponding to a pF^- value of 12.09 ± 1.5 agrees well with the pF^- value of 12.03 given in reference 22.

(24) Jenkins, H. D. B.; Roobottom, H. K.; Glasser, L. *Inorg. Chem.,***2003**, *42,* 2886.

(25) Jenkins, H. D. B.; Glasser, L., submitted for publication.

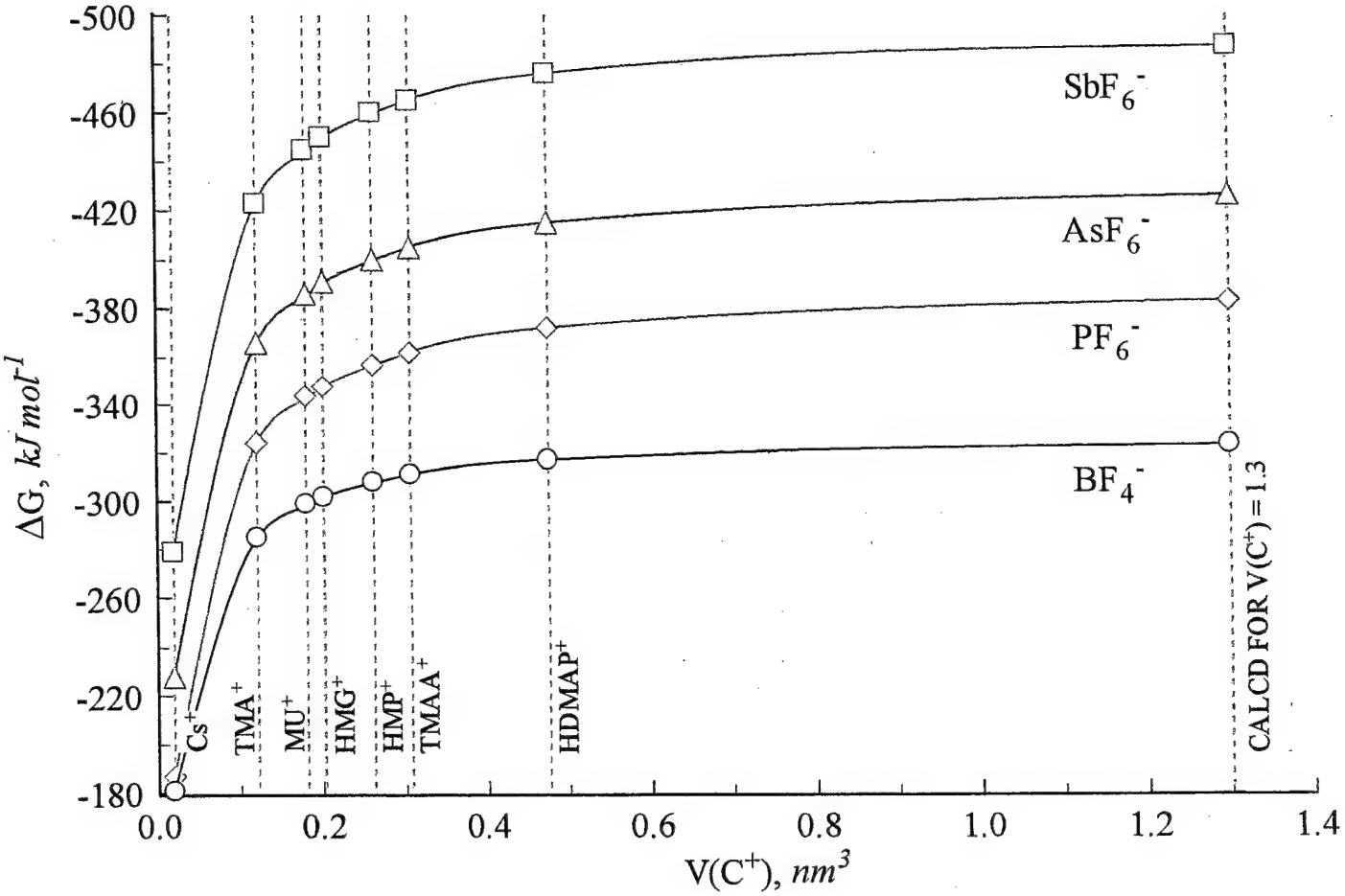
(26) Jenkins, H. D.B.; Tudela, D.; Glasser, L. *Inorg.Chem.*, **2002**, *41*, 2364.

(27) It should be noted that for salts with very large cations and small anions, the latter can fit into the holes in the cation-cation packing. Therefore in these cases, the additivity rule might no longer be valid. These considerations, however, in no way affect the conclusions in this paper.

Figure Captions

Figure 1. Plots of the free energy changes of reaction (1) against the molar volumes of cations I-VII and one hypothetical point with a molar volume of 1.3 nm^3, using SbF_5 (blue), AsF_5 (red), PF_5 (green), and BF_3 (black) as the acceptor molecules. For infinitely large molar volumes of the cation, the curves asymptotically approach the fluoride ion affinity values (+ *RT* terms) of the acceptors.

Figure 2. Plots of the "nakedness" parameters, $\{\Delta H - FIA + 3/2RT\}$, of the cations I-VII against their molar volumes and one hypothetical point with a molar volume of 1.3 nm^3. It can be seen that after correction of ΔH for 2/3RT and the F^- affinities of the corresponding F^- acceptors, the four curves of Figure 1 collapse into a single line, that asymptotically approaches zero for infinitely large molar volumes of the cation.


-500
-460
-420
-380
-340
-300
-260
-220
-180
ΔG, kJ mol-1
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
V(C+), nm3
SbF6-
AsF6-
PF6-
BF4-
Cs+
TMA+
MU+
HMG+
HMP+
TMAA+
HDMAP+
CALCD FOR V(C+) = 1.3

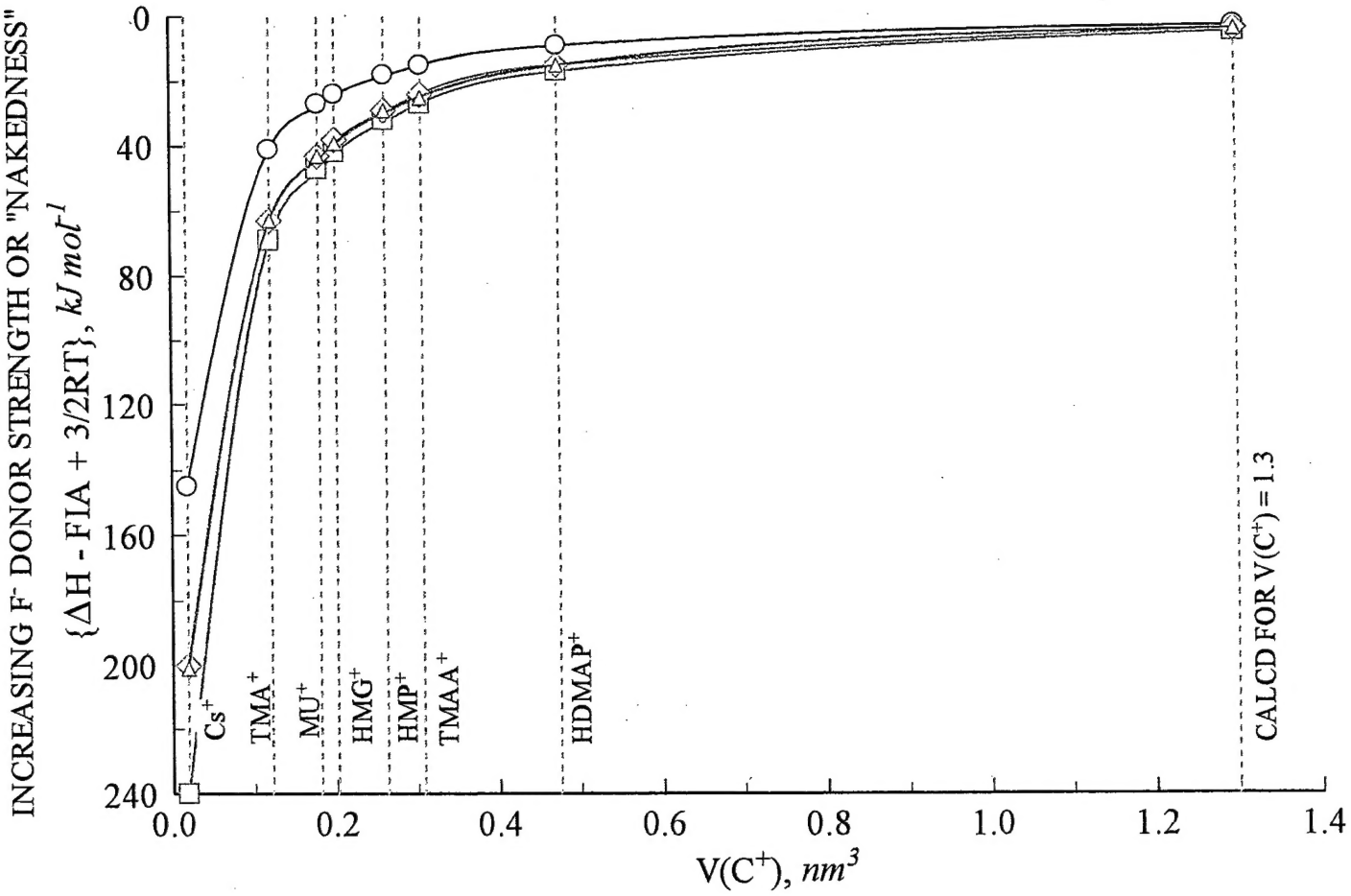
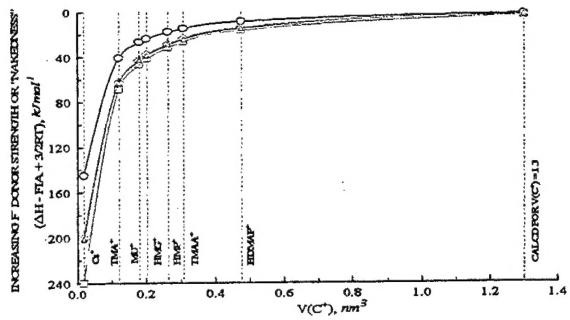

INCREASING F⁻ DONOR STRENGTH OR "NAKEDNESS"
{ΔH - FIA + 3/2RT}, kJ mol⁻¹
0
40
80
120
160
200
240
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
V(C⁺), nm³
Cs⁺
TMA⁺
MU⁺
HMG⁺
HMP⁺
TMAA⁺
HDMAP⁺
CALCD FOR V(C⁺) = 1.3

Table 1. Estimation of ΔG / kJ mol^{-1} from Born-Haber cycle and equation (2)[a]

	Cation	V(C+)	V(CF)	V(AF$^-$)	V(CAF)	U(CAF)	U(CF)	pF$^-$	FIA	ΔH	k(ΔV)[b]	S(A,g)	TΔS	ΔG	[ΔH – FIA + 3/2 RT][c]
		nm^3	nm^3	nm^3	nm^3	kJ mol^{-1}	kJ mol^{-1}	kcalmol^{-1}10^{-1}	kJ mol^{-1}	kJ mol^{-1}	JK^{-1}mol^{-1}	JK^{-1}mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
A=SbF$_5$															
	Cs	0.0188	0.0438	0.121	0.1398	556	769	12.03	-503	-294	-130.6	180.27	14.81	-279	240
	TMA	0.121	0.146	0.121	0.242	480	549	12.03	-503	-438	-130.6	180.27	14.81	-423	69
	MU	0.1807	0.2057	0.121	0.3017	454	501	12.03	-503	-460	-130.6	180.27	14.81	-445	47
	HMG	0.2021	0.2271	0.121	0.3231	446	488	12.03	-503	-465	-130.6	180.27	14.81	-450	42
	HMP	0.2624	0.2874	0.121	0.3834	427	459	12.03	-503	-475	-130.6	180.27	14.81	-460	32
	TMAA	0.3074	0.3324	0.121	0.4284	415	442	12.03	-503	-480	-130.6	180.27	14.81	-465	27
	HDMAP	0.4755	0.5005	0.121	0.5965	382	399	12.03	-503	-491	-130.6	180.27	14.81	-476	17
		1.3	1.325	0.121	1.421	312	317	12.03	-503	-502	-130.6	180.27	14.81	-487	5
A=BF$_3$															
	Cs	0.0188	0.0438	0.073	0.0918	623	769	8.31	-348	-207	-65.3	153.45	26.27	-181	145
	TMA	0.121	0.146	0.073	0.194	509	549	8.31	-348	-311	-65.3	153.45	26.27	-285	41
	MU	0.1807	0.2057	0.073	0.2537	474	501	8.31	-348	-325	-65.3	153.45	26.27	-299	27
	HMG	0.2021	0.2271	0.073	0.2751	465	488	8.31	-348	-328	-65.3	153.45	26.27	-302	24
	HMP	0.2624	0.2874	0.073	0.3354	441	459	8.31	-348	-334	-65.3	153.45	26.27	-308	18
	TMAA	0.3074	0.3324	0.073	0.3804	428	442	8.31	-348	-337	-65.3	153.45	26.27	-311	15
	HDMAP	0.4755	0.5005	0.073	0.5485	390	399	8.31	-348	-343	-65.3	153.45	26.27	-317	9
		1.3	1.325	0.073	1.373	314	317	8.31	-348	-349	-65.3	153.45	26.27	-323	3
A=PF$_5$															
	Cs	0.0188	0.0438	0.109	0.1278	569	769	9.49	-397	-201	-114.2	163.2	14.59	-187	200
	TMA	0.121	0.146	0.109	0.23	487	549	9.49	-397	-338	-114.2	163.2	14.59	-324	63
	MU	0.1807	0.2057	0.109	0.2897	458	501	9.49	-397	-358	-114.2	163.2	14.59	-344	43
	HMG	0.2021	0.2271	0.109	0.3111	450	488	9.49	-397	-363	-114.2	163.2	14.59	-348	38
	HMP	0.2624	0.2874	0.109	0.3714	430	459	9.49	-397	-372	-114.2	163.2	14.59	-357	29
	TMAA	0.3074	0.3324	0.109	0.4164	418	442	9.49	-397	-377	-114.2	163.2	14.59	-362	24
	HDMAP	0.4755	0.5005	0.109	0.5845	384	399	9.49	-397	-386	-114.2	163.2	14.59	-372	15
		1.3	1.325	0.109	1.409	313	317	9.49	-397	-397	-114.2	163.2	14.59	-383	4
A =AsF$_5$															

Cs	0.0188	0.0438	0.11	0.1288	568	769	10.59	-443	-246	-115.6	174.21	17.47	-228	201
TMA	0.121	0.146	0.11	0.231	486	549	10.59	-443	-384	-115.6	174.21	17.47	-366	63
MU	0.1807	0.2057	0.11	0.2907	458	501	10.59	-443	-404	-115.6	174.21	17.47	-386	43
HMG	0.2021	0.2271	0.11	0.3121	450	488	10.59	-443	-408	-115.6	174.21	17.47	-391	39
HMP	0.2624	0.2874	0.11	0.3724	430	459	10.59	-443	-418	-115.6	174.21	17.47	-400	29
TMAA	0.3074	0.3324	0.11	0.4174	418	442	10.59	-443	-422	-115.6	174.21	17.47	-405	25
HDMAP	0.4755	0.5005	0.11	0.5855	384	399	10.59	-443	-432	-115.6	174.21	17.47	-415	15
	1.3	1.325	0.11	1.41	313	317	10.59	-443	-443	-115.6	174.21	17.47	-426	4

[a] For all rows, 3/2 RT = 4 kJ mol^{-1}
[b] $\Delta V = V(C^+AF^-) - V(C^+F^-)$
[c] Quantitative parameter to measure "nakedness" of fluoride ion sources or donor strength

Quantitative Measure for the "Nakedness" of Fluoride Ion Sources

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